

Coordination Compounds of Cobalt, Nickel, Copper and Zinc with Thiosemicarbazone and 3-Phenylpropenal Semicarbazone

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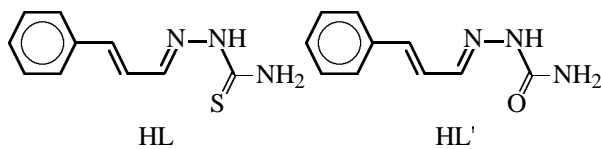
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Abstract—Hydrates of 3-phenylpropenal thiosemicarbazone (HL·H₂O) and semicarbazone (HL'·H₂O) react in methanol with cobalt, nickel, copper, and zinc chlorides, nitrates, and acetates to form coordination compounds MX₂·2HL·nSolv [M = Co, Ni, Cu, Zn; X = Cl, NO₃; HL = C₆H₅CH=CH-CH=N-NHC(O)NH₂; n = 0–3; Solv = H₂O, CH₃OH], CuX₂·HL·nH₂O [M = Ni, Cu; n = 0, 1], ML₂·nH₂O and ML'·nH₂O [M = Co, Ni, Zn; HL' = C₆H₅CH=CH-CH=N-NHC(O)NH₂; n = 0–3]. In the presence of amines (A = C₅H₅N, 2-CH₃C₅H₄N, 3-CH₃C₅H₄N, and 4-CH₃C₅H₄N) these reactions yield the complexes Cu(A)LCI·CH₃OH and M(A)LX·nH₂O [M = Cu, Ni; X = Cl, NO₃; n = 0–2]. The copper complexes with the amine ligands are of polynuclear structure, and other complexes are monomeric. Carbazones (HL and HL') are included in the complexes as bidentate N,S- and N,O-ligands. The thermolysis of the complexes involves the stages of removing solvent crystallization molecules (70–90°C), deaquation (150–170°C), and full thermal decomposition (500–580°C).

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Thiosemicarbazones and semicarbazones of aldehydes and ketones contain a wide set of donor atoms in the composition and form with transition metal ions coordination compounds of various composition, structure, and properties [1–5]. Many of them are biologically active, which allows their using as a basis for the creation of selectively operating microbiological nutrient media, potential disinfectants and antiseptic agents [6–10]. In this connection the synthesis and study of new complexes of biometals with such ligands is of the both scientific and practical interest.

The aim of the present work was to find optimal conditions for the synthesis of cobalt, nickel, copper, and zinc coordination compounds with 3-phenylpropenal thiosemicarbazone (HL) and semicarbazone (HL'), to determine their composition and structure, and also to study their physical and chemical properties.



It was shown experimentally that the reactions of hot (50–55°C) methanol solutions of cobalt, nickel,

copper, and zinc chlorides, nitrates, or acetates with HL or HL' carbazones in the molar ratio 1:2 give fine-crystalline compounds (I–VI, IX–XI, XIII, and XVI). On the basis of elemental analysis (Table 1) we propose for them the following compositions: $\mu X_2 \cdot 2HL \cdot nSolv$ [M = Co (I, II), Ni (III, IV), Cu (VI), Zn (IX); X = Cl (I, III, VI), NO₃ (II, IV, IX), M = 1 (VI), 2 (I–IV, IX); Solv = H₂O (II, IV, IX), CH₃OH (I, III, VI)], ML₂·nCH₃OH [M = Ni (V), Zn (X); n = 0 (X), 1 (V)] and ML'₂·nCH₃OH [M = Co (XI), Ni (XIII), Cu (XVI)]. If the reaction of an above-stated metal chloride is carried out with HL or HL' carbazone under study in the presence of either pyridine or 2-, 3-, or 4-picoline in the mole ratio 1:1:1 the corresponding complex is precipitated from the solution: Cu(A)LCI·C₃OH (VII, VIII) or M(A)L'CI (XII, XIV, XV, XVII–XX) [M = Co (XII), Ni (XIV, XV), Cu (XVII–XX); A = C₅H₅N (VII, XII, XVII), 2-CH₃C₅H₄N (XIV, XVIII), 3-CH₃C₅H₄N (VIII, XIX), and 4-CH₃C₅H₄N (XIV, XX)].

Complexes I–XX are insoluble in diethyl ether, slightly soluble in water, better soluble in alcohols, and readily soluble in DMF, DMSO, and acetonitrile. Their yields and certain physicochemical characteristics are given in Table 1.

It was possible to grow up single crystals of HL thiosemicarbazone and V, X complexes at the re-

Table 1. Physicochemical characteristics of cobalt, nickel, copper, and zinc coordination compounds (**I–XX**) with 3-phenylpropenal thiosemicarbazone (HL) and semicarbazone (HL')

Comp. no.	Yield, %	μ_{eff} , ^a BM	Found, %				Formula	Calculated, %			
			Cl	M ^b	N	S		Cl	M ^b	N	S
HL	68	^c	–	–	18.65	14.19	C ₁₀ H ₁₃ N ₃ O ₂ S	–	–	18.83	14.35
I	71	4.82	11.61	9.68	14.06	10.47	C ₂₂ H ₃₀ CoCl ₂ N ₆ O ₂ S ₂	11.75	9.77	13.91	10.60
II	69	4.97	–	9.31	18.09	9.99	C ₂₀ H ₂₆ CoN ₈ O ₈ S ₂	–	9.38	17.81	10.17
III	63	3.02	11.48	9.50	14.02	10.34	C ₂₂ H ₃₀ Cl ₂ N ₆ NiO ₂ S ₂	11.75	9.77	13.91	10.60
IV	58	2.90	–	9.68	18.06	10.40	C ₂₀ H ₂₆ N ₈ NiO ₈ S ₂	–	9.38	17.81	10.17
V	65	^c	–	11.55	16.97	12.58	C ₂₁ H ₂₄ N ₆ NiO ₂ S	–	11.82	16.83	12.83
VI	71	1.82	18.85	16.95	11.08	8.41	C ₁₁ H ₁₅ Cl ₂ CuN ₃ O ₂ S	19.09	17.20	11.29	8.60
VII	72	1.40	8.39	15.38	9.95	7.60	C ₁₆ H ₁₉ ClCuN ₄ O ₂ S	8.56	15.44	10.13	7.72
VIII	70	1.54	8.01	12.80	15.08	7.28	C ₁₇ H ₂₁ ClCuN ₄ O ₂ S	8.28	13.07	14.94	7.47
IX	69	^c	–	10.46	17.51	10.21	C ₂₀ H ₂₆ N ₈ O ₈ S ₂ Zn	–	10.23	17.64	10.08
X	55	^c	–	13.46	17.51	6.49	C ₂₀ H ₂₀ N ₆ S ₂ Zn	–	13.74	17.76	6.77
HL'	80	^c	–	–	20.11	–	C ₁₀ H ₁₃ N ₃ O ₂	–	–	20.29	–
XI	71	4.17	–	12.49	18.15	–	C ₂₁ H ₂₄ CoN ₆ O ₃	–	12.63	17.99	–
XII	68	4.33	10.04	16.18	15.28	–	C ₁₅ H ₁₅ CoClN ₄ O	9.82	16.32	15.49	–
XIII	78	4.66	–	12.69	17.70	–	C ₂₁ H ₂₄ N ₆ NiO ₃	–	12.63	17.99	–
XIV	70	4.84	9.31	15.50	15.09	–	C ₁₆ H ₁₇ ClN ₄ NiO	9.45	15.71	14.91	–
XV	77	4.52	9.16	15.59	14.65	–	C ₁₆ H ₁₇ ClN ₄ NiO	9.45	15.71	14.91	–
XVI	73	1.81	–	13.17	17.56	–	C ₂₁ H ₂₄ CuN ₆ O ₃	–	13.56	17.80	–
XVII	79	1.38	9.43	17.18	15.01	–	C ₁₅ H ₂₄ ClCuN ₄ O	9.69	17.46	15.28	–
XVIII	72	1.41	9.06	16.55	14.47	–	C ₁₆ H ₁₇ ClCuN ₄ O	9.33	16.82	14.71	–
XIX	66	1.54	9.11	16.61	14.60	–	C ₁₆ H ₁₇ ClCuN ₄ O	9.33	16.82	14.71	–
XX	78	1.58	9.16	16.69	14.44	–	C ₁₆ H ₁₇ ClCuN ₄ O	9.33	16.82	14.71	–

^a At 294 K. ^b M is metal. ^c A complex is diamagnetic.

crystallization of the substances under study from methanol. Their structures were determined by the X-ray crystal analysis. Crystals of HL are rhombic, a 6.227(1), b 7.763(2), and c 25.585(5) Å; β 90°, space group $P2_12_12_1$, Z 4, R 0.0426. The molecule of this azomethine is nonplanar and has E configuration. The crystals of complex **V** have triclinic syngony, a 6.551(2), b 10.752(3), and c 10.885(3) Å; α 64.751(5), β 82.753(5), γ 89.857(5); space group $P-1$, Z 1, R 0.1376. Its molecule contains a monomeric nickel complex, which is centrosymmetrical in relation to the metal atom. The central atom coordinates two deprotonated thiosemicarbazone (HL) molecules located in a trans-position through the imine nitrogen atom and the thioamide sulfur atom to form a distorted plane square. When coordinated to the metal atom, azomethine (HL) changes the E configuration in relation to the N¹–C² bond for the Z configuration.

The crystals of complex **X** are monoclinic, a 25.342(2), b 9.150(2), and c 21.340(3) Å; α 90, β 111.84(2), and γ 90°, space group $C2/c$, Z 8, R 0.0556. Two deprotonated bidentate thiosemicarba-

zones (HL) in its molecule are coordinated to a zinc ion through imine nitrogen atoms and thioamide sulfur atoms to form a distorted tetrahedral coordination polyhedron at the central atom. As well as in complex **V**, thiosemicarbazone (HL) changes the E configuration relative to the N¹–C² bond for the Z configuration on the coordination to a zinc ion. It was found that in the crystals of compounds (HL, **V**, **X**) under study the molecules are packed into infinite layers in parallel to the (0 0 1) and (0 1 0) planes.

The visual microscopic study of powdery coordination compounds **I–IV**, **VI–IX**, **XI–XX** showed that they possess phase uniformity and consist of crystallites of various forms. In view of small particle sizes and also because of the absence of single crystals of these compounds we proved the individuality of their composition and structure by elemental and thermal analyses, magnetochemistry, ¹³C NMR, and IR spectroscopy.

The determination of molar conductivity of the synthesized complexes in DMF showed that compounds **II**, **IV**, and **IX** are three-ion electrolytes (α

142–168 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and other substances are non-electrolytes (κ 2–6 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

On the basis of the magnetochemical data we found (Table 1) that all cobalt compounds are paramagnetic and, judging from effective magnetic moments, central atoms in thiosemicarbazone complexes **I** and **II** and in semicarbazone complexes **XI** and **XII** have a pseudo-octahedral and a tetrahedral structure, respectively, of the coordinated unit. Complexes **V** and **XIII** are diamagnetic, the other nickel compounds are paramagnetic and central atoms in their composition are in a tetrahedral ligand environment. The magnetochemical characteristics of copper compounds **VI** and **XVI** correspond to the spin value for one unpaired electron and point to their monomerism. As for copper complexes with amines and carbazones (HL and HL'), they have a polynuclear structure as their effective magnetic moments are underestimated in comparison with the spin value for one unpaired electron.

The thermal analysis of compounds **I–XX** (Table 2) showed that their thermolysis proceeds through the stages of desolvation (60–90°C), deaquation (155–180°C), or deamination (180–200°C) up to the complete thermal-oxidative destruction of a complex (370–585°C). The temperature (t) of the complete decomposition of a substance depends on the central atom nature and changes in the following sequence for coordination compounds with the same inner sphere composition: $t(\text{Zn}) > t(\text{Ni}) \geq t(\text{Co})$. The nature of inner-sphere ligands also affects the decomposition temperature of a substance: it increases on the replacement of an azomethine semicarbazide fragment by a thiosemicarbazide fragment, on the replacement of nitrate ions by chloride ions and of inner-sphere water by amine, and in the case of complexes with amines **VII**, **VIII**, **XIV**, **XV**, and **XVII–XX** with the same central ion in the sequence: $t(3\text{-CH}_3\text{C}_5\text{H}_4\text{N}) \geq t(4\text{-CH}_3\text{C}_5\text{H}_4\text{N}) \geq t(\text{C}_5\text{H}_5\text{N}) > t(2\text{-CH}_3\text{C}_5\text{H}_4\text{N})$. Using Horowitz–Metzger's method [11] with regard to Topor's additions [12] we estimated kinetic parameters of desolvation, deaquation, and deamination reactions of the complexes. The results obtained are given in Table 2, which shows that the activation energy (E_a) thus found and the pre-exponential factor (Z) are close to the kinetic parameters of the similar reactions described in the literature [13–15]. It was found that the E_a and $\log Z$ values for the second stage of thermolysis are affected by the nature of the central atom and the inner-sphere ligands and for the complexes of the same composition they change in the sequences $\text{Zn} > \text{Co} > \text{Ni}$ and $3\text{-CH}_3\text{C}_5\text{H}_4\text{N} > 4\text{-CH}_3\text{C}_5\text{H}_4\text{N} > \text{C}_5\text{H}_5\text{N} > 2\text{-CH}_3\text{C}_5\text{H}_4\text{N}$. These sequences coincide with the above-described series of the variation of complete decomposition temperatures of the sub-

stances and with the series of the basicity of amines. In the latter case a different sequence is observed only for 2- $\text{CH}_3\text{C}_5\text{H}_4\text{N}$, probably owing to steric hindrances.

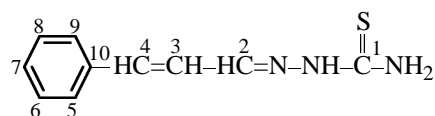
To determine coordination modes of the ligands with the central ions, we compared the IR spectra of complexes (**I–XX**), starting carbazones HL and HL', and also of coordination compounds of the transition metals with the similar Schiff bases described in the literature [1–3]. Azomethines HL and HL' in the compounds under study behave as bidentate electro-neutral or monodeprotonated N,S- or N,O-ligands bound to a complex-forming ion through azomethine nitrogen atoms and a sulfur or oxygen atom of a carbamide fragment to form a five-membered metal-containing ring. This conclusion is proved by the fact that $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ absorption bands are displaced to the low-frequency region by 25–15 cm^{-1} as compared to the similar absorption bands in the spectra of starting HL and HL' carbazones, where they are located at 1600–1592 and 770 cm^{-1} , respectively. The participation with the central atoms of sulfur or oxygen atoms, respectively, of HL and HL' ligands in the deprotonated thioenol or thiocarbamide form is confirmed by the disappearance of the absorption bands $\nu(\text{C}=\text{S})$ at 770 cm^{-1} , $\nu(\text{C}=\text{O})$ at 1660 cm^{-1} , and $\nu(\text{NH})$ at 3210–3200 and 3170–3150 cm^{-1} from the IR spectra of complexes **V**, **VII**, **VIII**, and **XI–XX**, and also by the appearance of new absorption bands in the field of 605–585 cm^{-1} , which, according to [16], are identified as $\nu(\text{C}-\text{S})$ and $\nu(\text{C}-\text{O})$, and also by splitting the band $\nu(\text{C}=\text{N})$ at 1595–1590 cm^{-1} into two components. The abovementioned coordination of HL and HL' carbazones is also supported by the fact that several new absorption bands appear in the region of 550–400 cm^{-1} [$\nu(\text{M}-\text{N})$ at 525–510 and 420–405 cm^{-1} , $\nu(\text{M}-\text{O})$ at 490–470 cm^{-1} , and $\nu(\text{M}-\text{S})$ at 460–445 cm^{-1}] in the IR spectra of all the complexes.

The participation of other functional groups of HL and HL' compounds in the coordination with metal ions is excluded, as their characteristic absorption bands lie in the same regions as for the starting carbazones. The presence of coordinated water and amine molecules in the complexes under study is proved by the presence of the corresponding absorption bands in their IR spectra [$\nu(\text{H}_2\text{O})$ 3590–3580, $\delta(\text{H}_2\text{O})$ 1580–1575, and $\gamma(\text{H}_2\text{O})$ 925–920 cm^{-1} in the case of aqua complexes **II**, **IV**, and **IX**, and $\nu(\text{CC}) + \nu(\text{CN}) + \delta(\text{CCH})$ 1640–1635 and 1530–1525, $\nu(\text{CN})$ 1310–1305, $\delta(\text{CCH})$ 1230–1225, $\delta(\text{CCH}) + \nu(\text{CC}) + \delta(\text{CNC})$ 1060–1055 and 1030–1025, $\gamma(\text{CCC}) + \gamma(\text{CNC})$ 730–725, $\rho(\text{CH})$ 830–825 cm^{-1}] for the complexes with amines **VII**, **VIII**, **XII–XIV**, and **XVII–XX**.

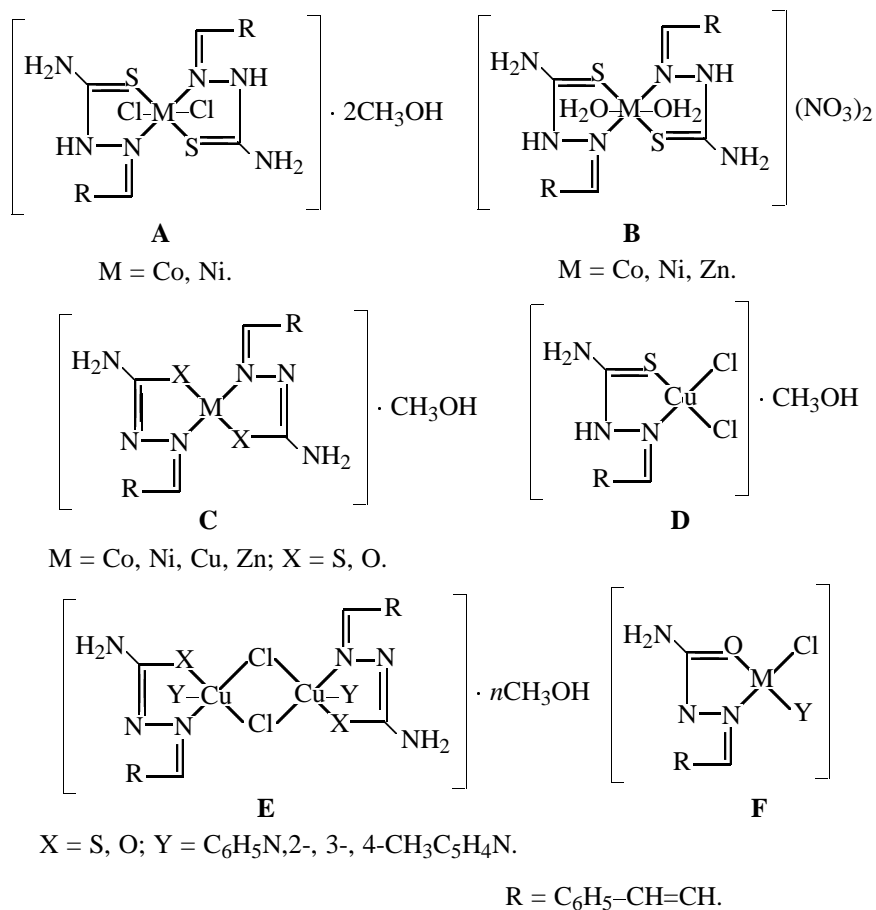
Table 2. Results of the thermal analysis of cobalt, nickel, copper, and zinc coordination compounds with 3-phenylpropenal thiosemicarbazone and semicarbazone **I–XX**

Comp. no.	Number of the endo-effects in DTA curve	Temperature of maximum effect, °C	Weight loss			Kinetic parameters		Temperature of full decomposition, °C
			found, %	calculated, %	corresponds to detachment of	E_a , kJ mol ⁻¹	log Z	
I	1	65	10.5	10.6	2CH ₃ OH	58.2	7.9	520
II	1	170	5.5	5.7	2H ₂ O	135.7	14.9	370
III	1	75	10.9	10.6	2CH ₃ OH	62.0	8.0	530
IV	1	155	6.0	5.7	2H ₂ O	130.5	14.4	380
V	1	60	6.0	6.4	CH ₃ OH	51.4	7.2	560
VI	1	65	9.0	8.6	CH ₃ OH	45.4	6.3	480
VII	1	60	7.9	7.7	CH ₃ OH	40.9	6.1	520
VIII	2	185	19.0	19.1	C ₅ H ₅ N	148.1	15.2	
	1	75	7.7	7.5	CH ₃ OH	42.1	6.2	530
IX	2	195	22.0	21.7	C ₆ H ₇ N	154.9	16.1	
	1	180	6.0	5.7	2H ₂ O	140.1	15.0	400
X	–	–	–	–	–	–	585	
XI	1	70	7.0	6.9	CH ₃ OH	40.2	6.0	440
XII	1	200	22.1	21.9	C ₅ H ₅ N	161.4	17.7	470
XIII	1	60	7.2	6.9	CH ₃ OH	41.3	6.2	450
XIV	1	175	25.0	24.8	C ₆ H ₇ N	145.8	15.1	460
XV	1	195	25.2	24.8	C ₆ H ₇ N	159.6	16.3	490
XVI	1	70	7.0	6.8	CH ₃ OH	40.6	6.1	410
XVII	1	180	22.0	21.6	C ₅ H ₅ N	146.8	14.9	430
XVIII	1	165	24.5	24.4	C ₆ H ₇ N	140.6	15.1	400
XIX	1	195	24.0	24.4	C ₆ H ₇ N	151.4	16.1	450
XX	1	185	24.1	24.4	C ₆ H ₇ N	148.9	15.9	440

To study behavior of the synthesized compounds in solutions, we investigated the ¹³C NMR spectra of nickel and zinc complexes with HL thiosemicarbazone. The experimental data obtained are presented in Table 3, which shows that the spectrum of HL thiosemicarbazone contain the signals of ¹³C atoms both in *sp*³ and *sp*² hybridizations. The signals are assigned according to [17]. The spectra of the complexes contain the signals characteristic of the thiocarbamide and thioenol forms of the coordinated ligand. In the case of complexes **IV** and **IX** containing the thiocarbamide form of the ligand the shifts referred to TMS are changed insignificantly compared to the free ligand, whereas the signals of C¹ and C² atoms of compounds **V** and **X** containing deprotonated thioenol form are shifted by 4–10 ppm. The position of the signal of C³ atom also varies upon the thiosemicarbazone coordination. It is necessary to note that complex **V** remains diamagnetic on dissolution, whereas in the case of coordination compound **IV** the resonance signals are strongly broadened pointing to its

Table 3. Assignment of signals in ¹³C NMR spectra of 3-phenylpropenal thiosemicarbazone (HL) and of zinc and nickel complexes with this ligand (**IV**, **V**, **IX**, and **X**), δ_C, ppm

Comp. no.	1	2	10	4	6, 7, 8	5, 9	3
HL	177.7	144.8	138.9	135.9	128.9	126.9	125.1
IV	177.0	143.2	137.2	134.1	127.2	125.2	123.4
V	173.8	155.7	141.4	135.5	129.7	127.5	120.0
IX	177.8	145.1	139.1	136.0	129.1	127.1	125.3
X	173.4	151.7	140.4	135.7	129.3	127.1	123.7



paramagnetism. Thus, our study showed that the coordination mode of thiosemicarbazone and the shape of the coordination unit do not change on the dissolution of the compounds under study.

Obtained physical and chemical data allow us to present the distribution of chemical bonds in complexes **I–XX** by the schemes **A–F**.

EXPERIMENTAL

The X-ray crystal analysis of compounds **HL**, **V**, and **X** was carried out on Philips PW-1100 and Bruker Smart diffractometers with a CCD-detector (MoK_α radiation, γ 0.71073 Å). The electric resistance of solutions of complexes **I–XX** in DMF (20°C, *c* 0.001 M) was measured with an R-38 slide-wire bridge. The IR spectra of the substances, which were initially stored in a dry chamber at 105°C to a constant weight, were recorded on a Specord M-80 spectrophotometer (samples as a suspension in Vaseline and fluorinated oils). The effective magnetic moments of compounds **I–XX** were determined by Gouy's method. We calculated the molar magnetic suscepti-

bility corrected for the diamagnetism on the basis of theoretical values of magnetic susceptibility of organic compounds. The derivatograms of complexes **I–XX** were recorded on a Paulik–Paulik–Erdey derivatograph in the range 20–1000°C in air (Al₂O₃ as a reference compound, corundum crucible). The ¹³C NMR spectra were recorded on a Bruker AC-400 spectrometer in DMSO-*d*₆ relative to TMS.

3-Phenylpropenal thiosemicarbazone hydrate (HL). A hot (55–60°C) alcohol solution containing 10 mmol of 3-phenylpropenal in 15 ml of methanol was mixed with a solution containing 10 mmol of thiosemicarbazide in 35 ml of CH₃OH. On cooling the reaction mixture, a light yellow precipitate was formed, which was filtered off on a glass filter, washed out by a small amount of alcohol and dried in air; mp 104–106°C.

Similarly, using 3-phenylpropenal and semicarbazide in the mole ratio 1:1 as starting substances, we synthesized semicarbazone **HL'**. The substance has mp 156–158°C.

Carbazones **HL** and **HL'** are readily soluble in DMF, DMSO, and, on heating, in alcohols.

Cobalt dichlorobis(3-phenylpropenalidenthiosemicarbazide) dimethanol-solvate. To a hot (50–55°C) solution of 10 mmol of cobalt dichloride hexahydrate in 20 ml of methanol 30 ml of an alcohol solution containing 20 mmol of 3-phenylpropenal thiosemicarbazone hydrate was added. The resulting reaction mixture was heated at continuous stirring for 25–30 min. A dark-brown substance was precipitated from the mixture on cooling, which was filtered off on a glass filter, washed out by a small amount of alcohol and ether, and dried in air up to a constant weight.

Similarly, using HL and HL' carbazones and cobalt, nickel, copper, or zinc chlorides, nitrates, or acetates as starting substances, we synthesized compounds **II–VI**, **IX–XI**, and **XIII–XVI**. Complexes **VII**, **VIII**, **XII**, **XIV**, **XV**, and **XVII–XX** were obtained according to the above-described technique by the reactions of salts and HL and HL' azomethines taken in the mole ratio 1:1 in the presence of pyridine and 2-, 3-, or 4-picoline (pH 8). Yields of compounds **I–XX** and their physical and chemical characteristics are given in Tables 1 and 2.

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